

Summary Sheet 2: Enols and Enolates

Name	Structure	Example	pKa ¹ of H
enol			17
ketone			20
aldehyde			21
ketone hydrate			21
enone			20
ketone hydrate/enol			20
aldehyde			20
Aldehyde = 1° alcohol Ketone = 2° alcohol Alkene = 3° alcohol			
ketone hydrate/enone			20
carboxylic acid			Note 1
acid anhydride			Note 2
anhydride			Note 3
enone			20

Note 1: The carbonyl acid is deprotonated first. Subsequent deprotonation of the α -carbon yields formic acid, which has a high activation barrier due to charge repulsion. It can be done, but it requires a very strong base.

Note 2: It is difficult to measure the pKa of these species due to their reactivity.

Source: P. H. Brügel, "Organic Chemistry"

Note that values of these values differ slightly from textbook by textbook and researcher to researcher; however, there is universal agreement that for a given structure, pKa increases in the order anhydride < ketone < enone < enol.

If you have a vastly different set of values, I would appreciate it if you brought it to my attention.

For a comprehensive list of pKa values see:

1) <http://www.hanschel.info/acidbase.htm>
2) <http://www.chem.utoronto.ca/~mch/acidbase.html>

Structural Features of the Carbonyl Group

- Catalytic oxygen w/ partialized δ -C=O bond angle $\sim 120^\circ$
- δ -C=O bond strongly polarized
- Carbonyl carbon is partially positive (electron delocalized)
- Large partial negative oxygen nearly nonpolar (well suited with strong both)

Key Concept: Resonance



Resonance: a form of isomerism where a lone pair moves to an oxygen through the movement of a proton and breaking of bonding electrons.

For acetone (CH_3CO_2) the total pKa value is ~ 20.0 (1.2730). The main reason is the difference in bond strengths between the two species.

The α -proton is most significant for ketones and anhydrides. (They may also encounter it with acid anhydrides in the mechanism of the Friedel-Crafts Claisen reaction). Enones and enolates are less acidic and most acidic exclusively at the carbonyl (e.g. $\text{CH}_2=\text{CH-C(=O)CH}_3$ has a pKa of 10.6, while for ethyl acetate

Acetone in D_2O will slowly incorporate deuterium at the α -carbon. The α -proton is responsible for this behavior. The rate of ketone deprotonation is greatly increased by CH_3CO_2 (base).

Five factors that influence the relative proportion of ketone/enol:

1. Aromaticity



2. Hydrogen bonding stabilizes the enol form



3. Strongly hydrogen bonding substituents can disrupt the dipole. The above equilibrium is 91:9 in favor of enol using water as solvent.

4. Conjugation is stabilizing



5. As with alkenes, increasing substitution increases α -hydrogen stability (assuming equal steric factors).

Effect on acidity of alkyl groups

The carbonyl is an electron-withdrawing system with partializing of electrons. It stabilizes adjacent negative charge.



Why the huge difference in acidity? The lone pair is stabilized by delocalization into the carbonyl system.



Questions: How do you explain the relative acidity of the following series?



Acetone: The more electron-poor the carbonyl, the greater will be its ability to stabilize negative charge. Conversely, the greater the increasing acidity of a substituent on the carbonyl, the less it will be able to stabilize negative charge.

The aromatic anhydride substitution pattern is a good proxy for the acidity of a functional group to donate to a carbonyl.



Substitution of the α -carbon by a benzene carbonyl derivative makes the α -carbon even more acidic.



The rate of resonance interconversion is greatly enhanced by acid. Acid makes carbonyls more nucleophilic, increasing acidity of α -protons, facilitating formation of enol. This increases K_a .



Net result: Addition of acid speeds proton exchange between the keto and enol forms.

Effect on reactivity of anions

Lesson: The presence of a carbonyl group activates anions toward nucleophilic attack.



The reactivity of the alkene toward nucleophilic attack is directly related to the stability of the enolate ion.



Can predict the results of the reaction by pKa?

Key Reaction: Enolate Formation



Important: the enolate is a NUCLEOPHILE!

Alkynyl anion and alkene anion are also nucleophiles in the reactions of α,β -unsaturated carbonyls.

Two key examples:



Claisen Condensation

The goal here is clarity and consistency: I would greatly appreciate feedback on any errors, omissions, or suggestions for improvements. Thank!

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